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Photoresponsive lower-rim azobenzene substituted and bridged calix[4]arenes

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Abstract

The doubly azobenzene-chain *lower-rim* substituted calix[4]arenes **6**–**9** were prepared, followed by the doubly bridged biscalix[4]arenes **10** and **11**. All are photoresponsive and detailed studies of the E ⇌ Z photoisomerization and the *Z*→*E* thermal isomerization in **6** and **10** were carried out using UV and ^{1}H NMR spectroscopic techniques. The three (*EE*, *EZ* and *ZZ*) isomers of **6** and **10** were isolated or enriched and fully characterized by ^{1}H NMR. Kinetic analyses of these transformations of **6** were carried out and revealed a concentration dependent behavior and an interesting sequential course of its photoisomerization.

Keywords: Bridged calixarenes; Azobenzene; Photoisomerization; Supramolecular chemistry

1. Introduction

Since McKervey, Böhmer et al. [1,2] have published in 1990, the first example of *lower-rim* bridged double calix[4]arenes, a number of structures of this type were reported [3–19] and the conformational implications were discussed. The studies featured crown[*n*]cavitand bridging units [3,4], mixed tetraethers [5] with conformational control and substituted 2,2′-bipyridine bridges [6,7] (which lead to barrel-shaped calix[4]arene podands and cryptands and their Eu^{3+}-complexes) and recently, a double calix[4]arene with four ethylene bridges [8,9] and high complexation selectivity towards potassium ions. Azobenzene substituted calixarenes are also known, within *upper-rim* arms [10–13] or *lower-rim* crown-ether bridges [14–19]. Notwithstanding the ample documentation on azobenzene moieties in a variety of host systems [10–28], there is relatively little known on the intimate details, in particular concerning the sequential manner of the photoisomerization processes in multiply azobenzene substituted systems. In our own quest for photoswitchable systems [20–24], (for critical appraisals and reviews of azobenzene photoisomerization, see: [25–28]) we report here the preparation of certain new *lower-rim* substituted and bridged calix[4]arenes **6**–**11**, and the results of detailed probes of their photoresponsive behavior, using selective irradiation techniques.

2. Experimental section

2.1. General

2.1.1. Synthesis

Solvents were purified and dried by standard methods prior to use. All reactions were carried out under an argon atmosphere. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AM 250 spectrometer (250 and 62.9 MHz, respectively). ^{13}C NMR assignments were made with the aid of DEPT-135 experiments. Mass spectra were obtained on a Micromass MALDI-TOF SpecE spectrometer using 9-nitroanthracene as the matrix. Microanalyses were performed by the microanalytical department of the Kekulé-Institut, University of Bonn. Thin-layer chromatography: TLC aluminium sheets, silica gel 60 F_{254} (Merck). Column chromatography: Silica gel 60, mesh size 63–100 μm (Merck).

2.1.2. Photochemistry

Photochemical experiments were performed on a JASCO CRM-FA Spectro-irradiator, equipped with a photon-counter. For quantum yields, the latter was periodically

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calibrated by chemical actinometry (using the Aberchiome 540 actinometer); at 338 nm the output was 2.5×10^{-8} einstein s^{-1}; the experimental data are in counts (1 count=4.2 s). The usual bandwidth for 1 cm cells was ±13 nm; when needed, this range was reduced by using narrower windows. The estimated error in quantum yield determinations is 15%. Irradiations were carried out, for both preparative and analytical purposes, at 338 nm. The solutions were prepared in the dark, otherwise, daylight photoisomerization was observed. All irradiations were performed on deoxygenated (Ar or N_2) acetonitrile solutions in quartz (<300 nm) or pyrex (300–500 nm) UV cells or NMR tubes. The products of the preparative runs at 338 nm were used for thermokinetic studies in NMR tubes held at constant temperatures, kept by reflux of various solvents. Both photochemical and thermochemical experiments were monitored using UV and/or ^{1}H NMR spectroscopy. UV spectra were measured on a UVIKON-931 spectrophotometer. NMR spectra were taken on Bruker AC-200 Cryospec and AC-360-WB spectrometers and listed in table form, to stress the consistency in the assignment process.

The crude photoproducts of preparative irradiations of both **6** and **10** were chromatographed on an enwrapped Silica gel column and handled in the dark. The products were eluted (PE/$CHCl_3$ 8:2–2:8) in the order *EE*, *EZ*, *ZZ*. The NMR spectra were then measured on practically pure *EE* and *ZZ* samples and 92% pure **6***EZ* and 33% **10***EZ* mixtures. The ^{1}H NMR spectra of the latter could be well resolved and all are assembled in Tables 1 and 2 for ready and instructive comparison.

General procedure for the preparation of **6**–**11**: (Yields and R_f-values apply to the *EE*-isomer).To a solution of 0.17 mmol calix[4]arene (**4** or **5**) in acetonitrile (25 ml) was added 0.19 mmol of powdered potassium carbonate. The resulting suspension was stirred for 30 min at room temperature. A solution of 0.35 mmol of **1** or **2** (in case of **3**, a suspension of 0.17 mmol) in acetonitrile (10 ml) was added dropwise. The mixture was refluxed for 3 days. After cooling to room temperature, the solvent was removed under reduced pressure. 0.2N HCl (50 ml) and ethyl acetate (50 ml) were added to the residue, the layers were separated and the aqueous layer was extracted two times with ethyl acetate (10 ml). The combined organic layers were washed with water (20 ml) and dried with sodium sulfate. Evaporation of the solvent yielded the crude orange product, which was subsequently purified by column chromatography.

25,27-Bis[(azobenzene - 4- yl)methoxy]calix[4]arene -26, 28-diol (**6**). From 72 mg (0.17 mmol) **4**, 96 mg (0.35 mmol) **1** and 26 mg (0.19 mmol) K_2CO_3. Yield: 51 mg (37%); Mp: 227–228°C; R_f=0.67 ($CHCl_3$); MS (MALDI-TOF), *m*/*z*: 835.13 [M^++Na], 851.14 [M^++K]; Anal. Calc. for $C_{54}H_{44}N_4O_4$: C, 79.78; H, 5.46; N, 6.89; Found: C, 79.57; H, 5.51; N, 6.84; ^{1}H NMR (250 MHz, $CDCl_3$, 20°C): δ=3.39 (d, *J*=13.0 Hz, 4 H), 4.35 (d, *J*=13.0 Hz, 4 H), 5.15 (s, 4 H), 6.67 (t, *J*=7.4 Hz, 2 H), 6.78 (t, *J*=7.5 Hz, 2 H), 6.93 (d, *J*=7.5 Hz, 4 H), 7.07 (d, *J*=7.4 Hz, 4 H), 7.37 (m, 6 H), 7.80 (br, 4 H), 7,82 (s, 2 H), 7.86 (d, *J*=8.4 Hz, 4 H), 7.96 (d, *J*=8.4 Hz, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 20°C): δ=31.7, 78.0 (CH_2), 119.5, 123.0, 123.5, 125.8, 128.1, 128.1, 129.1, 129.3, 131.0 (CH), 128.7, 133.3, 139.8, 152.0, 152.5, 152.7, 153.5 (C_q).

5,11,17,23-Tetra(tert-butyl)-25,27-bis[(azohenzene-4-yl) methoxy]calix[4]arene-26,28-diol (**7**): From 110 mg (0.17 mmol) **5**, 96 mg (0.35 mmol) **3** and 26 mg (0.19 mmol) K_2CO_3. Yield: 86 mg (49%); Mp: 263–265°C; R_f=0.35 ($CHCl_3$/*c*-hexane 2/1); MS (MALDI-TOF), *m*/*z*: 1059.52 [M^++Na], 1076.48 [M^++K]; Anal. Calc. for $C_{70}H_{76}N_4O_4$: C, 81.05; H, 7.38; N, 5.40; Found: C, 81.22; H, 7.30; N, 5.24; ^{1}H NMR (250 MHz, $CDCl_3$, 20°C): δ=0.97 (s, 18 H), 1.29 (s, 18 H), 3.31 (d, *J*=13.2 Hz, 4 H), 4.32 (d, *J*=13.2 Hz, 4 H), 5.17 (s, 4 H), 6.82 (s, 4 H), 7.06 (s, 4 H), 7.36–7.39 (in, 6 H), 7.80–7.87 (in, 8 H), 7.98 (d, *J*=8.3 Hz, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 20°C): δ=31.2, 31.9 (CH_3), 31.7, 77.7 (CH_2), 123.0, 123.4, 125.2, 125.7, 128.0, 129.1, 130.9 (CH), 34.0, 34.1, 127.8, 132.7, 140.2, 141.6, 147.3, 149.9, 150.8, 152.4, 152.7 (C_q).

Table 1
^{1}H NMR data of the three isomers of **6** (200 MHz, $CDCl_3$/TMS, δ_{ppm}, multipl., J_{Hz})

Integr., position	**6***EE*	**6***ZZ*	**6***EZ*[a]	
			E chain	*Z* chain
2 H, OH	7.82, s	7.52, s	7.62, s	7.62, s
4 H, azo-H_{ar}	7.96, d (8.4)	7.45, d (8.4)	7.97, d (8.3)	7.47, d (8.3)
4 H, azo-H_{ar}.	7.86, d (8.4)	6.89, d (8.4)	7.79, d (83)	6.87, d (8.3)
4 H, azo-$H_{o\text{-}ar}$	7.80, bd	6.90, dm	7.97, bd	6.81, bd
6 H, azo-$H_{m,p\text{-}ar}$	7.37, m	7.14, tt (7.5, 1.0)	7.53, tt (7.4, 1.0)	7.17, tt
		7.25, tt (7.4, 1.0)	7.49, tt (7.4, 1.0)	7.07, tt
4 H, calix-H_{ar}	7.07, d (7.4)	7.05, d (7.5)	7.05, d	7.04, d
4 H, calix-H_{ar}	6.93, bd (~7.5)	6.85, bd (~7.5)	6.89, d (7.5)	6.85, d (7.5)
2 H, calix-H_{ar}	6.78, dd (8.0, 6.8)	6.73, dd (8.4, 6.4)	6.76, dd (7.5)	6.73, dd (7.5)
2 H, calix-H_{ar}	6.67, t (7.4)	6.68, t (7.5)	6.66, t (7.4)	6.66, t (7.4)
4 H, O–CH_2	5.18, s	5.01, s	5.14, s	5.00, s
4 H, calix-CH_2	4.35, d (13.0)	4.15, d (13.2)	4.31, d (13.1)	4.19, d (13.2)
4 H, calix-CH_2	3.39, d (13.0)	3.25, d (13.2)	3.37, d (13.1)	3.27, d (13.2)

[a] The high-field signals of **6***EZ* are presented in two separate *E* and *Z* columns.

Table 2
^{1}H NMR data of the three isomers of **10** (200 MHz, $CDCl_3$/TMS, δ_{ppm}, multipl., J_{Hz})

Integr., position	**10***EE*	**10***ZZ*	**10***EZ*[a]	
			E chain	*Z* chain
4 H,OH	8.20, s	7.68, s	7.96, s	7.96, s
8 H, azo-H_{ar}	7.96, d (8.2)	7.65, d (8.2)	7.98, d (8.3)	7.67, d (8.3)
8 H, azo-H_{ar}	7 77, d (8.2)	6.97, d (8.2)	7 95, d (8 3)	6.93, d (8.3)
8 H, calix-H_{ar}	7 10, d (7.4)	7.05, d (7.4)	7.08, d (7.5)	7.07, d (7.5)
8 H, calix-H_{ar}	6.99, d (7.4)	6.89, d (7.4)	6.96, d (7.5)	6.94, d (7.5)
4 H, calix-H_{ar}	6.83, dd (8.2, 6.8)	6.78, dd (8.4, 6.6)	6.82, bt (7.5)	6.81, bd (7.5)
4 H, calix-H_{ar}	6.68, t (7.4)	6.65, t (7.4)	6.67, t (7.5)	6.67, t (7.5)
8 H, O–CH_2	5.16, s	4.98, s	5.15, s	5.00, s
8 H, calix-CH_2	4.42, d (13.0)	4.32, d (13.0)	4.40, d (13.0)	4.37, d (13.0)
8 H, calix-CH_2	3.48, d (13.0)	3.40, d (13.0)	3.52, d (13.0)	3.42, d (13.0)

[a] The high-field signals of **10***EZ* are presented in two separate *E* and *Z* columns.

25,27-Bis[(4-methyl-azobenzene-4′-yl)methoxy]calix[4] arene-26,28-diol (**8**): From 72 mg (0.17 mmol) **4**, 101 mg (0.35 mmol) **2** and 26 mg (0.19 mmol) K_2CO_3. Yield: 36 mg (23%); Mp: 199–203°C; R_f=0.59 ($CHCl_3$); MS (MALDI-TOF), *m/z*: 841.45 [M^+], 864.42 [M^++Na], 881.23 [M^++K]; Anal. Calc. for $Cs_6H_{48}N_4O_4{\cdot}C_6H_{10}O_3$: C, 76.68; H, 602; N, 5.77; Found: C, 76.65; H, 5.89; N, 6.07; ^{1}H NMR (250 MHz, $CDCl_3$, 20°C): δ=2.39 (s, 6 H), 3.40 (d, *J*=13.2 Hz, 4 H), 4.36 (d, *J*=13.2 Hz, 4 H), 5.18 (s, 4 H), 6.69 (t, *J*=7.4 Hz, 2 H), 6.75 (t, *J*=7.4 Hz, 2 H), 6.92 (d, *J*=7.4 Hz, 4 H), 7.09 (d, *J*=7.4 Hz, 4 H), 7.17 (d, *J*=8.3 Hz, 4 H), 7.73 (d, *J*=8.3 Hz, 4 H), 7.85 (d, *J*=8.3 Hz, 4 H),7.86 (s, 2 H), 7.97 (d, *J*=8.3 Hz, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 20°C): δ=21.6 (CH_3), 31.6, 78.0 (CH_2), 119.1, 123.0, 123.3, 125.7, 128.0, 128.6, 129.2, 129.6 (CH), 128.0, 133.6, 139.6, 141.6, 151.0, 152.2, 152.8, 153.7 (C_q).

5,11,17,22-Tetra(tert-butyl)-25,27-bis[(4-methyl-azobenzene-4′-yl)methoxy]calix[4]arene-26,28-diol (**9**): From 110 mg (0.17 mmol) **5**, 101 mg (0.35 mmol) **2** and 26 mg (0.19 mmol) K_2CO_3. Yield: 33 mg (18%); Mp: 118°C; R_f=0.56 ($CHCl_3$); MS (MALDI-TOF), *m/z*: 1064.73 [M^+], 1089.72 [M^++Na], 1104.82 [M^++K]; Anal. Calc. for $C_{72}H_{80}N_4O_4{\cdot}C_6H_{10}O_3$: C, 77.91; H, 7.74; N, 4.78; Found: C, 78.07; H, 7.45; N, 4.92; ^{1}H NMR (250 MHz, $CDCl_3$, 20°C): δ=0.98 (s, 18 H), 1.31 (s, 18 H), 2.40 (s, 6 H), 3.32 (d, *J*=13.2 Hz, 4 H), 4.33 (d, *J*=13.2 Hz, 4 H), 5.17 (s, 4 H), 6.83 (s, 4 H), 7.07 (s, 4 H), 7.17 (d, *J*=8.1 Hz, 4 H), 7.19 (s, 2 H), 7.74 (d, *J*=8.1 Hz, 4 H), 7.84 (d, *J*=8.5 Hz, 4 H), 7.97 (d, *J*=8.5 Hz, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 20°C): δ=21.7, 31.2, 31.9 (CH_3), 31.7, 77.4 (CH_2), 123.1, 123.2, 125.2, 125.7, 128.1, 129.7 (CH), 34.0, 34.1, 127.8, 130.8, 132.7, 139.9, 141.2, 141.6, 147.3, 149.9, 150.8, 152.5 (C_q).

25,25′:27,27′-Bis(*p*-azotolyl-α,α′,ω,ω′-tetraoxy)dicalix[4] arene-26,26′,28,28′-tetraol (**10**): From 72 mg (0.17 mmol) **4**, 63 mg (0.17 mmol) **3** and 26 mg (0.19 mmol) K_2CO_3. Yield: 34 mg (32%); Mp: 264°C; R_f=0.69 ($CHCl_3$); MS (MALDI-TOF), *m/z*: 1283.47 [M^++Na], 1300.44 [M^++K]; Anal Calc. for $C_{84}H_{68}N_4O_8{\cdot}C_6H_{10}O_3$: C, 77 68, H, 5.65; N, 4.03; Found: C, 77.97; H, 533, N, 407; ^{1}H NMR (250 MHz, $CDCl_3$, 20°C): δ=3.48 (d, *J*=13.0 Hz, 8 H), 4.42 (d, *J*=13 0 Hz, 8 H), 5 16 (s, 8 H), 6.83 (d, *J*=7.4 Hz, 4 H), 6.68 (t, *J*=7.4 Hz, 4 H), 6.99 (d, *J*=7.4 Hz, 8 H), 7.10 (d, *J*=7.4 Hz, 8 H), 7.77 (d, *J* = 8.2 Hz, 8 H), 7.96 (d, *J*=8.2 Hz, 8 H), 8.20 (s, 4 H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 20°C): δ=31.9, 78.2 (CH_2), 119.4, 123.7, 126.2, 127.8, 128.9, 129.6 (CH), 128.0, 133.6, 140.0, 152.1, 152.5, 153.8 (C_q).

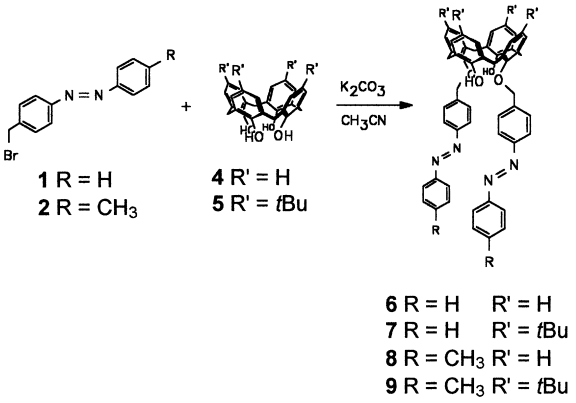
5,5′,11,11′,17,17′,22,22′-Octa(tert-butyl)-25,25′:27,27′-bis(*p*-azotolyl-α,α′,ω,ω′-tetraoxy)dicalix[4]arene-26,26′,28, 28′-tetraol (**11**): From 110 mg (0.17 mmol) **5**, 63 mg (0.17 mmol) **3** and 26 mg (0.19 mmol) K_2CO_3. Yield: 43 mg (30%); Mp: 233–236°C; R_f=0.86 ($CHCl_3$); MS (MALD1-TOF), *m/z*: 1731.08 [M^++Na]; Anal. Calc. for $C_{116}H_{132}N_4O_8{\cdot}C_6H_{10}O_3$: C, 79.62; H, 7.78; N, 3.04; Found C, 79 46; H, 7 83; N, 3.07; ^{1}H NMR (250 MHz, $CDCl_3$, 20°C): δ=1.01 (s, 36 H), 1.27 (s, 36 H), 3.39 (d, *J*=13.0 Hz, 8 H), 4.38 (d, *J*=13.0 Hz, 8 H), 5.13 (s, 8 H), 6.90 (s, 8 H), 7.07 (s, 8 H), 7.76 (s, 4 H), 7.83 (d, *J*=8.4 Hz, 8 H), 7.92 (d, *J*=8.4 Hz, 8 H); ^{13}C NMR (62.9 MHz, $CDCl_3$, 20°C): δ=31.4, 31.1 (CH_3), 32.3, 77.9 (CH_2), 123.6, 125.4, 126.1, 127.8 (CH), 34.2, 34.4, 127.7, 133.13, 140.4, 141.8, 147.7, 150.1, 151.2, 152.6 (C_q).

3. Results and discussion

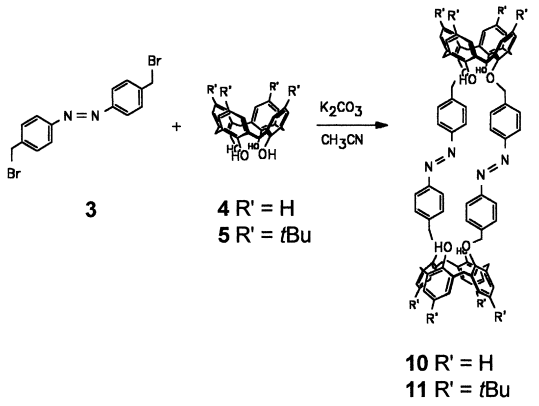
3.1. Synthesis

The reaction of two equivalents of the starting materials 4-(bromomethyl)azobenzene **(1)** or 4-(bromomethyl)-4′-methylazobenzene (**2**) [29–31] with calix[4]arenes **4** or **5** in acetonitrile, in the presence of potassium carbonate, provided the 25,27-substituted calix[4]arenes **6**–**9**, in their *EE* form (Scheme 1).

In a similar way, the use of 4,4′-bis(bromomethyl)azobenzene (**3**) [29–31] and calix[4]arenes **4** or **5** in equimolar ratios, afforded the new macrocyclic compounds **10** and **11** (Scheme 2). Efforts to prepare a fourfold bridged double calix[4]arene from two equivalents of **3** with either **4** and **5** or **10** and **11**, using NaH in DMF, did not yield the expected products. Apparently, the azobenzene residue is sterically



Scheme 1. Synthesis of the *lower-rim* doubly substituted calix[4]arenes (**6**–**9**).



Scheme 2. Synthesis of the *lower-rim* doubly bridged calix[4]arenes (**10**,**11**).

too demanding, to allow fourfold flanking. It is worth noting that no high dilution conditions are necessary in this cyclization step, indicating a favorable geometry and entropy of activation of the open intermediate.

3.2. Photochemistry

25,27-Bis(4-oxymethyleneazobenzene)calix[4]arene-26, 28-diol in its native *EE* form (**6***EE*) [λ_{max}, nm (ε): 224 (47,000), 287 (23,000), 320 (35,000), 437 (1500)] was irradiated in its various absorption bands (Fig. 1). The effective irradiation wavelengths were in the 311–365 nm range, causing **6***EE*→**6***EZ*+**6***ZZ* photoisomerization, as monitored by ^{1}H NMR (Table 1). At 338 nm, a photostationary state with better than 90% of the **6***ZZ* isomer was reached and the concentration of **6***EZ*was about four times that of the residual **6***EE*, as measured in the high-field ^{1}H NMR spectrum of the photoproduct (cf. Fig. 2-bottom). Low wavelength irradiation (257 nm) gave other, photodegradation products (which were not further pursued) and at 284 nm, a mixture of those and the *E*–*Z* photoisomerization products was obtained. The quantum yields for disappearance of **6***EE* at 338 (Fig. 3), as well as at 365 nm were ϕ(**6**)=0.05, both in concentrated solution (as measured by NMR and UV), and in dilute one (by UV); corrections were needed with the concentrated solution, for disobeying the Beer–Lambert law and with the dilute one, for total absorption. Four isosbestic points at 380, 273, 237 and 216 nm were observed in this process, much to our surprise, because of the anticipated intermediacy of **6***EZ* in any **6***EE*⇌**6***ZZ* interconversion. There can be a linear relationship in the concentrations of **6***EE* and **6***ZZ* only if the **6***EZ* concentration is constant and low, or if the discrete absorption coefficients of the azo-chains in the isomeric species are additive (*E* in *EE* and *EZ* or *Z* in *EZ* and *ZZ*) and the rate of disappearance of the (overall) *E* chains is equal to the rate of formation of *Z* chains. To examine this process we carried out a careful kinetic ^{1}H NMR study, using the well-separated high field signals of **6***EE*, **6***EZ* and **6***ZZ* (Fig. 2 and Table 1).

Fig. 4 delineates the gained information in graphical form. In Fig. 4, Graphs 1 and 4 show that the disappearance rate of **6***EE* in the sequence **6***EE*→**6***EZ*→**6***ZZ* is equal to the rate of

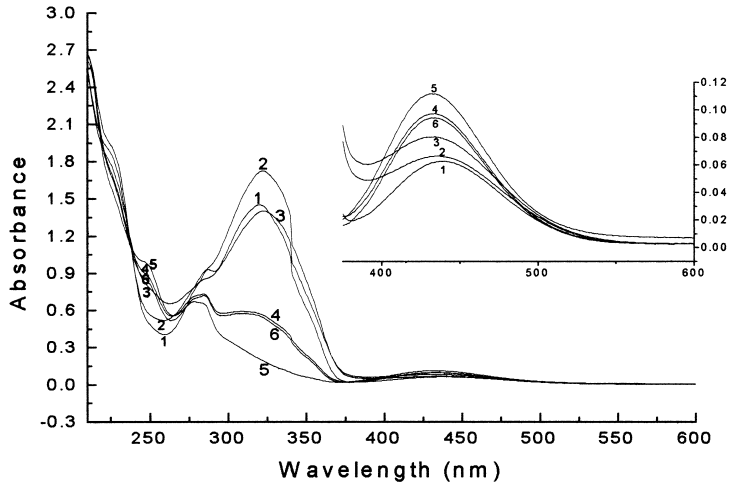


Fig. 1. Irradiation of **6***EE* (Spectrum 1) in MeCN (4.14×10^{-5}M) at various wavelengths: 2–257, 3–284, 4–311, 5–338 and 6–365 nm.

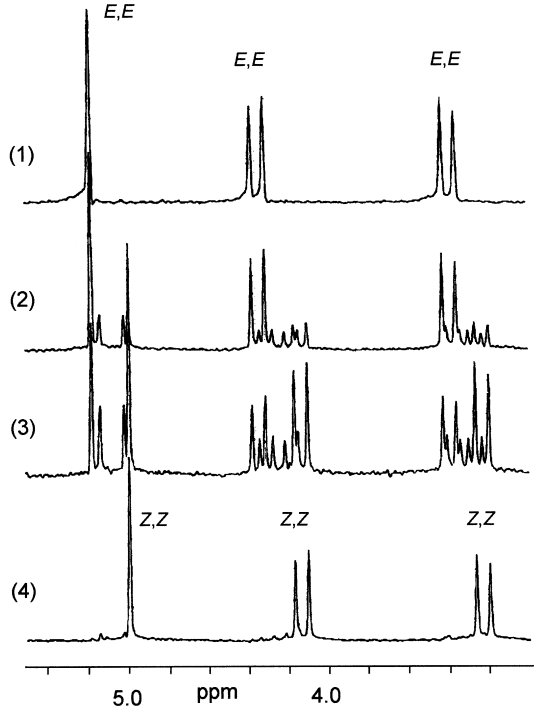


Fig. 2. High field ^{1}H NMR spectra of the 338 nm irradiation products of **6***EE* (1) in $CDCl_3$, down to the photostationary product (>90% **6***ZZ*) (4); cf. Table 1.

concomitant formation of **6***EZ*+**6***ZZ*. Graph 2 depicts the interesting, plateau-like shaped, evolution of **6***EZ* in the course of the reaction, and Graph 3, the formation of **6***ZZ*. Hence, no other products are involved in this sequential photoisomerization and, in the context of the isosbestic points, the **6***EZ* concentration is constant (after the first quarter of the process) but not low. A plot of the disappearance of *E* chains versus the formation of *Z* chains (Fig. 5) shows a slope of

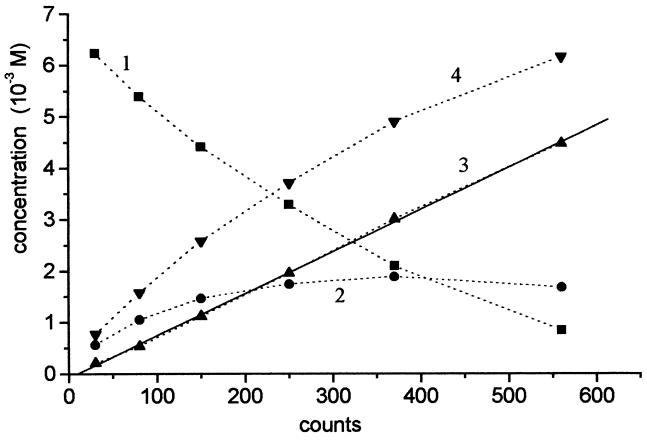


Fig. 4. Kinetic studies of the photoisomerization sequence **6***EE*→**6***EZ*→**6***ZZ*: (1)disappearance rate of **6***EE*; (2) the rise and fall of **6***EZ*; (3) rate of formation of **6***ZZ* (experimental: dotted, linear fit: full line, r=0.9996); (4) rate of formation of **6***EZ*+**6***ZZ*.

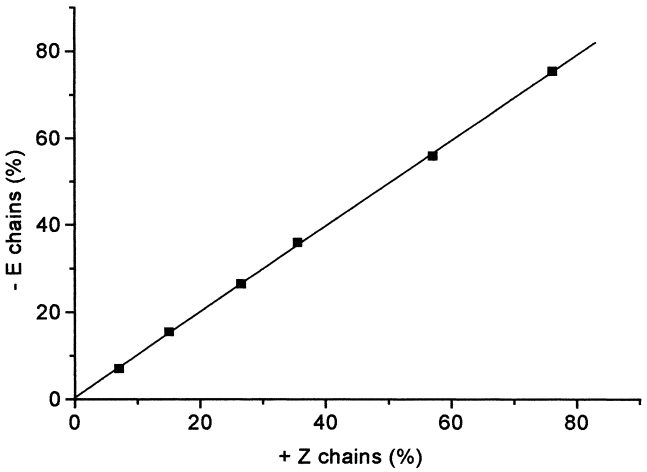


Fig. 5. Rate of disappearance of *E* chains vs. that of formation of *Z* chains in the irradiation of **6***EE* (r=0.9999).

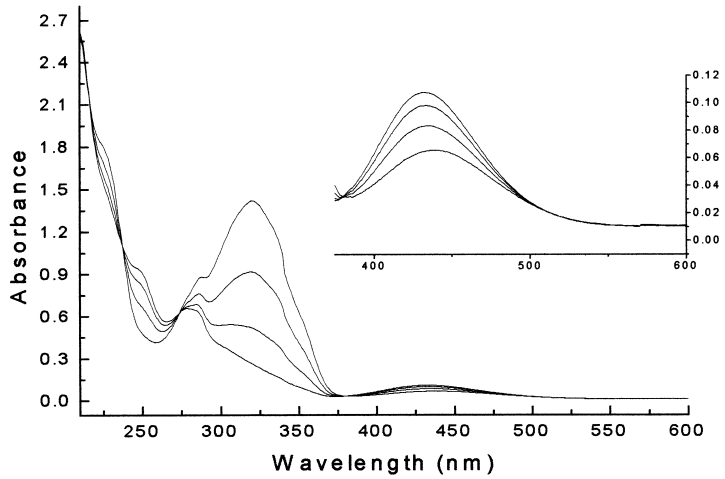


Fig. 3. UV monitored irradiation of **6***EE* in MeCN at 338 nm for quantum yield determination and isosbestic points.

1. This explains the isosbestic points as stemming from the phototransformation $E \rightarrow Z$, in which the behavior of the *E* chains is independent of the nature of the parent molecules (**6***EE* or **6***EZ*) containing them. The rate of formation of **6***ZZ* is linear all along the process (Fig. 4, Graph 3). That **6***ZZ* originates from **6***EZ* only and not from both **6***EE* (directly) and **6***EZ* can be concluded from: (i) the light absorption of **6***EZ* (in the concentrated NMR solution) is more than OD=1, when the concentration of **6***EZ* has reached 2% of the total; (ii) the rate of disappearance of **6***EE* is virtually equal to the rate of formation of **6***ZZ*, after the latter reached a concentration of 15% and the concentration of **6***EZ* remained constant (Fig. 4, Graphs 1 and 3); and (iii) the lines in Fig. 4 (Graphs 1 and 4) have practically equal slopes.

The *ZZ* form (**6***ZZ*) [λ_{max}, nm (ε): 247 (∼24,000), 285 (∼16,000), 278 (∼16,000), 432 (∼2700)] was irradiated in dilute solution at 446 nm, causing nearly total reversal to **6***EE*. We could not achieve pure **6***EE*, even by prolonged irradiation (at 446 or 419 nm) of a concentrated solution (3.3×10^{-3}M). A conjecture (following a more detailed analysis) for the failure of the full **6***ZZ*→**6***EE* phototransformation in these conditions, is the apparent occurrence of aggregates in concentrated solutions, with *Z* chains (of **6***EZ*) inside, shielded from light. Indeed, when a concentrated solution, consisting of 70% of **6***EE*, 27% of **6***EZ* and 3% of **6***ZZ*, was diluted and irradiated at 419 nm, we measured an increase of about 7% in OD at 320 nm, meaning that further 15% of **6***EZ* were converted to **6***EE*.

The thermal isomerization sequence **6***ZZ*→**6***EZ*→**6***EE* was measured by (high field) ^{1}H NMR in $CDCl_3$. **6***ZZ* disappears at 55°C, with a first order rate constant of $k_1 = 8.5 \times 10^{-3}\,\text{min}^{-1}$, $t_{1/2} = 81$ min The subsequent *Z* to *E*-chain isomerization in **6***EZ* was, however, much slower. Thus, after 5 h, the **6***ZZ* concentration was very low, which enabled us to undertake chromatographic separation of these isomers and to obtain a 93% pure **6***EZ* sample. The thermal isomerization **6***EZ*→**6***EE* (at 55°C) could thus be readily followed and gave $k_1 = 4.0 \times 10^{-3}\,\text{min}^{-1}$, $t_{1/2} = 173$ min.

25,25′:27,27′-Bis[4,4′-di(oxymethylene)azobenzene]-dicalix[4]arene-26,26′,28,28′-tetraol in its native *EE* form (**10***EE*) [λ_{max}, nm (ε): 229 (75,000), 279 (28,000), 287 (32,000), 328 (55,000), 445 (1500)] was submitted to an irradiation mapping study (Fig. 6), in the 257, 284, 311, 338 and 365 nm bands in THF. The irradiation at 338 and 365 nm was $E \rightarrow Z$ effective, while the 257 and 284 nm irradiations gave other (photodegradation) photoproducts (vide supra). At 338 nm, a photostationary state of 4% **10***EE*, 28% **10***EZ* and 68% **l0***ZZ* was reached. The quantum yield was determined by UV both on concentrated solutions and dilute ones (with suitable corrections, vide supra) (Fig. 7). Thus, at 338 and 365 nm, ϕ(**10**)=0.02 and three isosbestic points where observed, at 388, 280 and 295 nm. The occurrence of isosbestic points in such cases is reasonable [32,33], only if there is a linear relationship in the concentration of *overall E and Z chains*; **10***EZ* may be then either very short lived at this wavelength or have similar rates of formation and disappearance, that is, a low and constant concentration (see discussion above on the photochemical behavior of **6**).

The *ZZ*-isomer (**10***ZZ*) [λ_{max} nm, (ε): 278 (>29,000), 285 (<28,000), 446 (>3500)] was irradiated at 446 nm (in the above photostationary-state solution, 68%), which caused nearly total reversal to **10***EE*. Complete **10***ZZ*→**10***EE* reversal could be achieved by heating, $k_1 = 0.021\,\text{min}^{-1}$; $t_{1/2} = 32$ min at 52°C (by NMR).

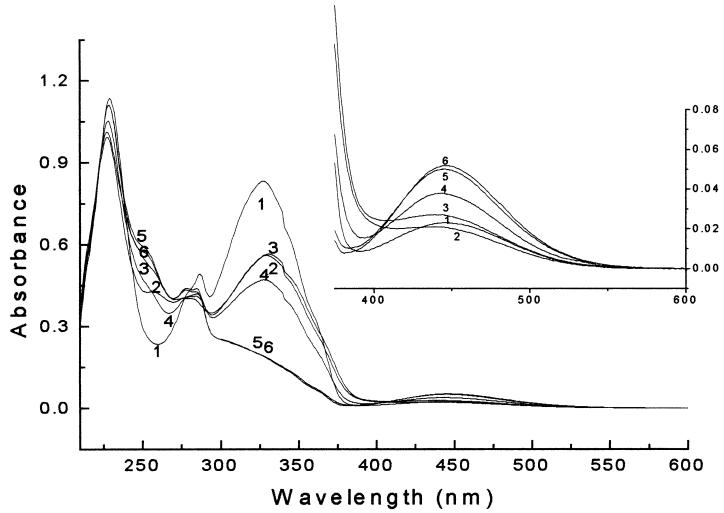


Fig. 6. Irradiation of **10***EE* (Spectrum 1) in THF (4.14×10^{-5}M) at various wavelengths: 2–257, 3–284, 4–311, 5–338 and 6–365 nm.

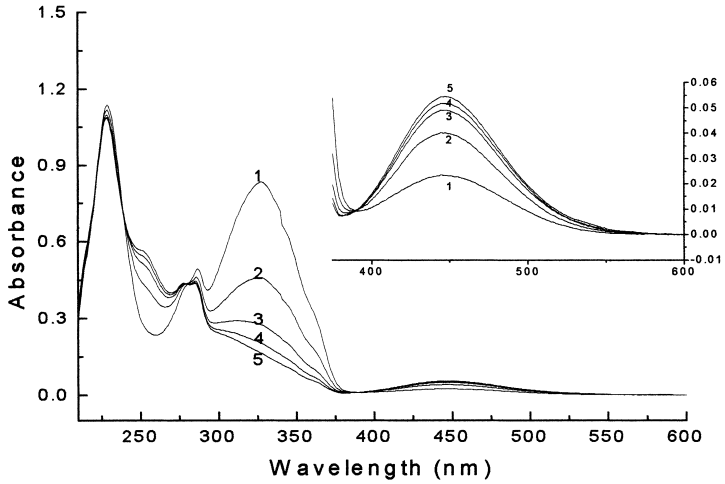


Fig. 7. UV monitored irradiation of **10***EE* in THF (365 nm) for quantum yield determination and isosbestic points.

4. Conclusions

We have prepared and characterized a series of new calix[4]arenes **6**–**9** doubly substituted on the *lower-rim* with azobenzene moieties and two bis(calix[4]arenes) **10** and **11**, similarly doubly bridged via their *lower-rim*. These are photoresponsive systems by virtue of the *E–Z* photoisomerizing azobenzene components and the three (*EE*, *EZ* and *ZZ*) isomers of each, **6** and **10**, could be either separated or enriched and characterized by ^{1}H NMR. Detailed kinetic studies of the thermo- and photochemical transformation of **6** revealed a concentration dependent behavior and an interesting sequential course of its photoisomerization. Cage type compounds of type **10** are being examined for photochemically driven recognition processes.

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